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ON THERMO-FLUCTULATION DESCRIPTION OF CHEMICAL REACTIONS IN POLYMERS

Investigations of polydienes with various chemical structures and microstructures were carried out, and interrelations of molecular-structural characteristics of polydienes with their macroscopic properties in thermo-oxidation processes were shown. An experimental-formal approach to substantiation of cross-linking and destruction depth of carbon-chain linear polydiene macromolecules is proposed. The extrapolation value of the molecular weight of the chain ensuring activation of chemical reactions of vulcanization and oxidation was obtained. It is proposed to use the criterion of destruction for calculating the number of chain splinters resulting from macromolecule ruptures.

Introduction. The ability of polymers to undergo chemical reactions is determined by their composition, nature of bonds forming the macromolecule main chain and lateral (side) groups and by the presence of active functional compounds in the structure of the chain or lateral (side) groups. Practical importance of studying polymer chemical reactions is that they can provide information on the possibility to improve properties of high-moleculer compounds at processing and application, on chemical transformations and technology of production and application of items.

Chemical reactions of polymers occur (proceed) under definite condition of external physical factors – temperature, pressure, deformation etc. Temperature as a measure of heat motion intensity determines the possibility of the system change to another state and provides the required energy. Mechanisms of inner energy transfer in polymers can be considered to be thermo-fluctuation processes which take account of relaxation - kinetic behavior of molecules under temperature effect. The thermo-fluctuation approach to the description of chemical reactions in polymers is based on the familiar physical knowledge that heat fluctuations of atoms result in rupture of chemical bonds, at first "weak" ones, and subsequent destruction of strong ones [1–2]. Temperature rise leads to higher probability of thermo-fluctuation dissociation of chemical bonding in the macromolecule, i.e. there increases the probability of formation of primary ruptures – defects in the polymer structure.

The given approach in investigating processes of cross-linking and destruction of elastomers provide for new ways to explain the course and nature of chemical reactions in elastomer systems with macromolecule activation centres.

Main part. Description of the structure and properties of rubber at oxidation ageing was paid much attention to [3–4], but substantiation of thermo-fluctuation knowledge on chemical reactions of polydienes at vulcanization requires additional investigations.

Molecular-structural characteristics of liquid polydienes capable to be vulcanized at lowered temperatures (about 60°C) were studied, commodity and specially synthesized polybutadienes with the molecular weight (MW) from 700 to 38,000 units (Table 1) were investigated.

Table 1

Structure and properties of liquid polydienes

Type of rubber	Content of links, %		MW	MWD
	1,4-*cis*	1,2-links		
LMPB	75–80	3–5	38,000	12.5
LMPB-N	78–82	3–5	35,000	11.0
SRDN-L	78	5	12,000	10.0
PBN1	75	5	4,000	2.3
PBN2	72	7	3,500	2.3
PBN2	73	5	2,500	2.1
SRDN-L	76	9	1,500	2.2
PBN4	74	6	1,100	2.0
PBN5	73	5	700	1.8

Compositions containing phosphorus (10.0), thiuram (3.0), captax (3.0), diphenylguanidine (3.0) were heated in alluminium containers in the thermostat defining hardness of 6 mlm samples Shore A (H_A). The starting time of cross-linking was recorded by the induction period time τ_U – time of the beginning of hardness increase which change in the course of the experiment characterizes the kinetics of liquid polydiene vulcanization (Fig. 1).

Heating at temperatures 60–100°C resulted in cross-linking of the samples under analysis, except PBN5, in delaying the beginning (Fig. 1 – extension of the induction period) and reducing the degree (maximal hardness) of vulcanization at decrease of both temperature and molecular weight of polybutadienes. These regularities were more vivid at 60°C.

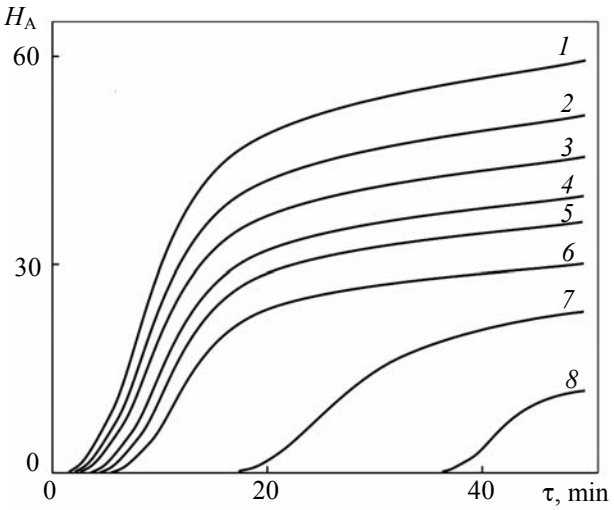

Fig. 1. Change of hardness Shore A of compositions based on oligobutadienes in vulcanization at 60°C: *1* – LMPB; *2* – LMPB-L; *3* – SRDNS; *4* – PBN1; *5* – PBN2; *6* – PBN3; *7* – SRDNL; *8* – PBN5

The graphic dependence $\tau_U = f(MW)$ (Fig. 2) provided for the extrapolation value M_{lim} = 2,000 which defines polybutadiene macromolecule length L_{lim}, and when it overincreases at 60°C there occurs a more effective cross-linking of liquid rubber. The assumption that cross-linking of oligobutadienes occurs through their primary thermofluctuation dissociation allows to conclude that M_{lim}corresponds to the statistically probable chain segment which ensures its initial rupture with subsequent sulfur joining to macromolecules.

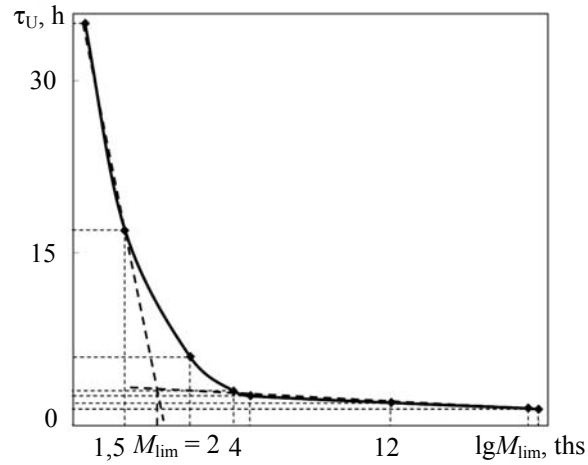

Fig. 2. Induction period τ_i of vulcanization of oligobutadiens with various molecular weights at 60°C

The calculations showed that this critical *MW* is equal to the number of butadiene monomer chains n_{lim} = 2,000 : 54 = 37 in the macromolecule. Taking into account the Kuhn dimensions of segment *s* = 7 of monomer chains [5] it can be assumed that at $M_{lim} \geq 5s$ and temperature 60°C in polybutadiene there occur (begin) thermo-fluctuation processes resulting in chemical reactions of sulfur-accelerating groups with oligodiene.

The discussed mechanism of butadiene cross-linking is confirmed by decrease (at the expense of destruction) and further increase (due to intermolecular reactions) of molecular weights of high-molecular polydienes at vulcanization. Here at oligobutadiene film heating there successively occur principal thermo-fluctuation transformations of 1,4-structures into CH_2-fragments of chains and/or there occur other processes with participation of cis-1,4-chains. The infrared spectra of oligodienes at their reaction with sulfur didn't show any stripes of absorption corresponding to CO- and OH-groups.

We consider it possible to apply the information on M_{lim} for substantiation of thermodestruction of carbon-chain linear polydienes. If we present the mean statistic probability N_p of such rupture occurrence in the form of a curve $N_p = f(MW)$, the starting point of its rise corresponds to value M_{lim} (Fig. 3) and the plateau is a mean statistic length $L_p(M_p)$ of the chain splinters which are the result of dissociation of the analyzed polymer macromolecules under the effect of initial thermofluctuations.

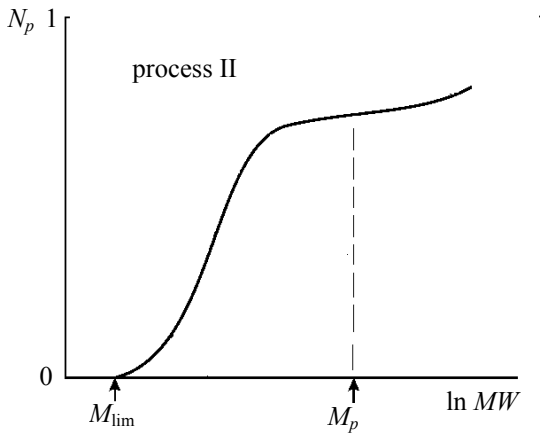

Fig. 3. Mean statistic probability of chain rupture N_p at polydiene molecular weight increase

Value $L_p = M_p$, perhaps, is the chain length where probably occurs at least one act of formation of a stable product of initial thermofluctuation rupture of macromolecules. The obtained results somehow clarify the increase of the chain splinters number at the increase of polymer molecular weights: the longer is the chain, the larger is the permissible number of macromolecule defects.

Division of the initial $MW = M_n$ into M_p allows to get the criterion of destruction h_g which value will become higher when the macromolecule becomes longer (Table 2).

On the basis of the principle of relative comparison and using the equation [6] Mark-Kuhn-Houwink

$$[\eta] = KM^{\alpha}$$

the following formula is proposed:

$$h_d = \frac{M_0}{M} = \sqrt[\alpha]{\frac{[\eta]_0}{[\eta]}},$$

where h_d – criterion of destruction from measurement of characteristic viscosity; d – constant of equation MKH ($a_m = 0.75$ – mean value on calculating 35 points "polymer-solvent"); [η] – characteristic viscosity of samples, initial and current.

Table 2

Criteria of destruction h_d of commodity polydiene films (20 μm) (calculation by equation MKH)

Rubbers with initial characteristic viscosity	Temperature of heating, °C			
	80	100	120	140
NR $[\eta]_0$ = 5.7 dl/g	2.2	2.8	3.2	3.6
SKI-3 $[\eta]_0$ = 4.1 dl/g	1.5	2.2	2.5	2.7
SKIL $[\eta]_0$ = 4.7 dl/g	1.6	2.3	2.4	2.5
SRDn $[\eta]_0$ = 3.2 dl/g	1.5	1.9	2.5	3.0
SRDt $[\eta]_0$ = 2.3 dl/g	1.2	1.2	1.3	1.4
SRDL $[\eta]_0$ = 2.5 dl/g	1.2	1.4	1.5	1.6

The merit of the criterion is that it allows to compare the efficiency of destruction (and structurization at $h_d < 1$) of various polymers in various chemical reactions and under various conditions.

Calculations of M_p by equation

$$M_p = M_\eta / h_d$$

can be applied for assessment of any molecular-structural changes of linear polymers in various stages and conditions of chemical reactions. Table 3 presents the calculated characteristic of elastomer thermodestruction products at 100°C with the use of criterion h_d from the data in Table 2.

The analysis of the data testifies to the fact that the order of value M_p for polyisoprenes approximately coincides, as for polybutadienes there occurs some excessive increase of value M_p in more regular titanium SBR with a larger molecular weight.

Table 3

Calculated values of molecular weight with average viscosity of polydiene oxidation products (at 100°C)

Rubber	M_η, ths.	Substrate KBr	Glass, 20 μm	Crumb
		M_p, ths.	M_p, ths.	M_p, ths.
NR	865	256	247	577
SKI-3	665	226	179	511
SDRn	298	157	137	221
SDRt	438	225	173	334

It should be taken into account that M_p (L_p), N_p are mean statistic values. Thus, it is believed that there may occur reduction (decrease) of probability of formation of reaction products with lower or higher than M_p values of the molecular weight.

All changes in the depth of destruction are conditioned by some factors. Firstly, the degree of initial material purity – addition of antiageing reagents [7] contributes to reduction of Δ[η], i. e. they increase M_p or degree of preservation of polydiene molecular weight and properties. Besides, use of various batches of rubber can define unmonitored changes of h_d. Secondly, the grade of polymers under investigation – polydienes have a higher value of h_g than that of ethylpropelene copolymers [8]. Thirdly, conditions of making the experiment – carbo-chain polymer films are thermooxidized according to h_g to a less extent than their extrudates [9]. Thus, two successive reactions should be observed (in polydienes) at increase of the molecular weight:

1) intermonomer destruction of the chain segments with $M_n = MW >> M_{\lim}$. It results in statistically probable splinters of macromolecules M_p with the 1% yield for polybutadienes at 60°C. This permits to assert that even in case of complete binding of each splinter of the chain by oxygen, its amount will be comparable with errors in application of most methods for determination of bound oxygen in organic polymers;

2) thermo-oxidative – oxidestruction of the chain segment with mean statistically probable $MW = M_p$. This presumes accumulation of energy on a shorter segment of polydiene macromolecules.

Since temperature rise in chemical reactions contributes to intensification of polymer destruction, values L_p and M_p determine the value of criterion h_d which increases at temperature rise. And the formal approach to substantiating h_d as the depth of macromolecule destruction determines intrinsic (essential) differences in the number of splinters (i. e. values L_p and M_p) in the middle and after reactions in polydienes. Temperature rise from 80 to 140°C leads to increase of h_d, i.e. to decrease of L_p and M_p. However, the assumption about intrinsic differences in the length L_p of the macromolecule segment before its statistically probable rupture M_p in two successive processes – polydiene intermonomer and oxidation destruction, requires further investigations and substantiations.

Difference in energies of various chemical bonds determines various variants of macromolecule thermofluctuation destruction. Intermonomer C-C-bonds are the weakest in polydienes. This determines a two-step change (reduction) of the molecular weight at thermo-oxidation: the first rupture of chains is conditioned by intermonomer macromolecule destruction, and the second – by the thermo-oxidation one.

The rupture of chains occurs mainly in imperfect – weak places of 1,4-cis-trans-1,2-(3,4)-intermonomer passes with concentration of thermofluctuation energy.

Conclusion. Prevalence of chain ruptures over their cross-linking is a total result of macromolecule thermofluctuation dissociation at the starting point of any (including vulcanization) chemical process in polymers. We ascertain that the initial thermofluctuation rupture of linear macromolecule "weak" bonds with a subsequent transfer of reactions to stronger chemical bonds can be viewed as the initial step of a chemical reaction in any polymer system.

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